Structural and magneto-transport properties of electrodeposited bismuth nanowires

Kai Liu and C. L. Chien[a)]
Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218

P. C. Searson
Department of Materials Science and Engineering, The Johns Hopkins University, Baltimore, Maryland 21218

Kui Yu-Zhang
Département de Physique, Université de Marne La Vallée, 5, Bd. Descartes/Champs sur Marne, 77454 Marne La Vallée Cedex 2, France

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Arrays of semimetallic Bi nanowires have been successfully fabricated by electrodeposition. Each nanowire consists of elongated Bi grains along the wire direction. Very large positive magnetoresistance of 300% at low temperatures and 70% at room temperature with quasilinear field dependence has been observed. These features are desirable for wide-range field sensing applications. © *1998 American Institute of Physics.* [S0003-6951(98)00236-8]

Recently, there has been considerable interest in fabricating nanostructured materials such as multilayers,[1] nanowires,[2–6] and nanoparticles,[7] as well as other composite materials.[8] Electrodeposition has the attractive features of cost-effectiveness, simplicity in operation, and the ability of deposition onto substrates with complex geometries.[9] In the case of nanowire arrays, electrodeposition is the only method with which such structures have been successfully fabricated.

Arrays of nanowires are a new type of nanostructures that exhibit quasi-1D characteristics. Because of high aspect ratios, small dimensions, and large quantities of wires, fabrication of nanowire arrays by vacuum deposition and patterning techniques are impractical. However, they can be electrodeposited into nanopores in suitable insulating media, such as polycarbonate, mica, or glass. The composition, morphology, and structure of the nanowires can be manipulated by growth parameters such as species, concentration, pH value of the electrodeposition bath, and deposition current density, etc. Previously, single-element metallic nanowires,[2,3] multilayered nanowires,[4–6] and alloy nanowires[10] have been fabricated by electrodeposition. They have already exhibited a rich variety of novel properties, including localization, perpendicular magnetic anisotropy, enhanced coercivity, and giant magnetoresistance (GMR).

To date, the constituent materials of the nanowires, and indeed magnetic nanostructures in general, consist mostly of transition metals, alloys, and noble metals. In this work, we report the successful fabrication of semimetallic Bi nanowires in which we have observed positive magnetoresistance (MR) as high as 300% at low temperatures and 70% at room temperature, with a quasilinear field dependence. In previous studies of negative GMR in metallic nanostructures,[11,12] the effect size is generally on the order of a few to a few tens of percent, except in nearly perfect superlattices which show the largest GMR effect of about 150% at 4.2 K.[13] The MR effect in the present semimetallic nanostructures not only has a much larger magnitude, but also is characteristically different.

Semimetallic Bi, with a rhombohedral structure, exhibits many unique electronic properties due to the small effective mass, the low density and the long mean free path of the carriers. There has been a long-standing interest in Bi nanostructures for both fundamental understanding and device applications. For example, the pursuit of quantum effects such as the semimetal–semiconductor transition in Bi thin films has continued to attract attention.[14–16] To date, most of the Bi nanostructures are in thin film form. However, fabrication of high quality Bi thin films through traditional vapor deposition has proven to be technically challenging. The properties of Bi thin films fabricated by vapor deposition depend sensitively on the purity and the concentration of crystal defects. These difficulties are further compounded by the low melting point of Bi and the possibility of the Bi thin films to have a distorted structure in which most of the unusual electronic properties are severely compromised. Nanowires of Bi described in this work offer a new medium for fabricating Bi nanostructures, for studying their unique electronic properties including finite-size effects, and for realizing large positive magnetoresistance (MR).

The electrodeposition process of the Bi nanowire is similar to those reported earlier.[3,6] Polycarbonate membranes (Nuclepore) were used as the template for the Bi nanowires. A layer of Au sputtered onto the bottom side of the membrane served as the working electrode in a standard three-electrode electrochemical cell. The electrolyte contained 75 g/l bismuth nitrate pentahydrate, 65 g/l potassium hydroxide, 125 g/l glycerol, and 50 g/l tartaric acid. The deposition solution was buffered to $p\mathrm{H}=0.90$ with nitric acid. The deposition was carried out at -30 mV relative to the $\mathrm{Ag}^+/\mathrm{AgCl}$ reference electrode, with Pt serving as the counter electrode. The nanowires thus made are typically up to 10 μm in length, arranged in a parallel manner. The diameter of the wire ranges from tens of nanometers to microns, and the

[a)]Electronic mail: clc@pha.jhu.edu

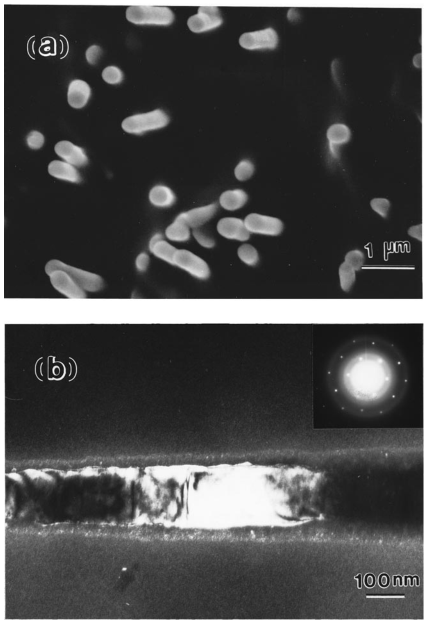

FIG. 1. (a) Top-view SEM image of 400 nm Bi nanowires with the supporting polycarbonate membrane partially removed. (b) Dark-field TEM image of a single 200 nm Bi nanowire. The inset shows the electron diffraction pattern taken from one of the grains.

number density varies from 10^4 to 10^7 wires/mm^2.

Structure and morphology of the Bi nanowires have been characterized by several methods. X-ray diffraction of the Bi nanowires revealed a rhombohedral structure, the same as that of bulk Bi, with no preferred orientation. Scanning electron microscopy (SEM) confirmed the expected arrangement of arrays of nanowires in parallel. Figure 1(a) shows the top-view SEM image of the 400 nm nanowires with the polycarbonate membrane partially removed, revealing that the nanowires are cylindrical in shape formed by the nanopores of the membrane. Transmission electron microscopy (TEM) provided further details of the nanowires. Figure 1(b) shows the dark-field TEM image of a single 200 nm wire removed from the membrane. The long Bi grains, typically two to four times that of the wire diameter, are separated by grain boundaries. The inset in Fig. 2(b) shows an electron diffraction pattern taken from one of the grains. The three-fold symmetry reveals a rhombohedral trigonal axis [111] along the wire direction. The close resemblance to the diffraction pattern of a cubic [111] zone axis demonstrates that the Bi rhombohedral lattice is indeed close to a slightly distorted cubic lattice. Along the nanowire, the diffraction patterns of different grains indicate different orientations, consistent with the polycrystalline structure shown by x-ray diffraction. The nanowires have also been confirmed to be pure Bi by energy dispersive x-ray microanalysis.

For transport measurements, the top side of the membrane was coated with another layer of Au after the deposition of the nanowires. Both Au layers were then patterned in order to make electrical contact to a smaller number of Bi nanowires.[6] The electrical resistance of the samples measured were typically on the order of 1–10 Ω. In zero magnetic field, the temperature dependence of the resistance of Bi nanowires with various diameters of 200 nm, 400 nm, and 2 μm are shown in Fig. 2. In all three cases, the resistance

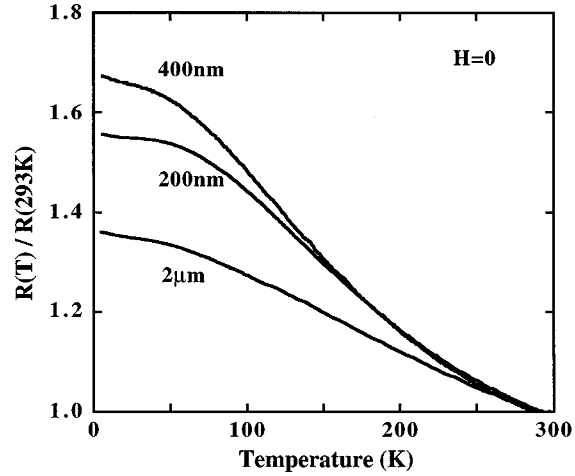

FIG. 2. Normalized temperature dependence of the resistance in zero magnetic field of the Bi nanowires with diameters of 200 nm, 400 nm, and 2 μm.

increases with decreasing temperature, i.e., the temperature coefficient of resistance (TCR) is negative. The ratio of resistance at 5 and 293 K, $R(5\text{ K})/R(293\text{ K})$, are in the range of 1.3–1.7. However, the negative TCR is not exponential, which is characteristic for semiconductors and insulators. In bulk Bi, the TCR is positive, while negative TCR is usually observed in Bi thin films.[14–16] This is because the main contributions to the TCR in Bi are due to carrier concentration and mobility, which have opposite temperature dependence. With increasing temperatures, the carrier concentration increases, whereas the carrier mobility decreases, leading to respectively a negative and a positive TCR. The competition between these two opposing contributions ultimately determines the TCR of a Bi sample. In bulk Bi, the carrier mobility dominates, thus a metallic-like positive TCR is seen. In Bi thin films, however, the carrier mobility is suppressed by structural imperfections and probably finite-size effects, leading to a negative TCR due to the carrier concentration. In the present case of Bi nanowires, because of the polycrystalline nature of the material, and the smaller wire diameter in comparison with the mean free path, the TCR is generally negative.

We next describe the MR effect in Bi nanowires. The MR has been measured with the magnetic field parallel (longitudinal MR) and perpendicular (transverse MR) to the nanowires. For the 400 nm Bi nanowires at 300 K shown in Fig. 3(a), a positive transverse MR of about 70% and a longitudinal MR of 40% is realized in a magnetic field up to 50 kOe. Note that the transverse MR in Bi nanowire is always larger than the longitudinal MR. Furthermore, the magnetic field dependence of MR, quadratic at low fields, becomes linear at higher fields, and shows no sign of saturation. Under field cycling, the MR shows no hysteresis. At lower temperatures, the field dependence of MR remains qualitatively the same, but the size of the MR effect becomes even larger. In the case of 400 nm wires at 32 K, MR of 300% has been observed, and its field dependence is shown in Fig. 3(b).

The positive GMR of Bi is the result of unusual characteristics of the carriers under the ordinary MR effect, which is the curving of the electron trajectory by a magnetic field. The characteristic quantity is $\omega_c\tau$, inversely proportional to

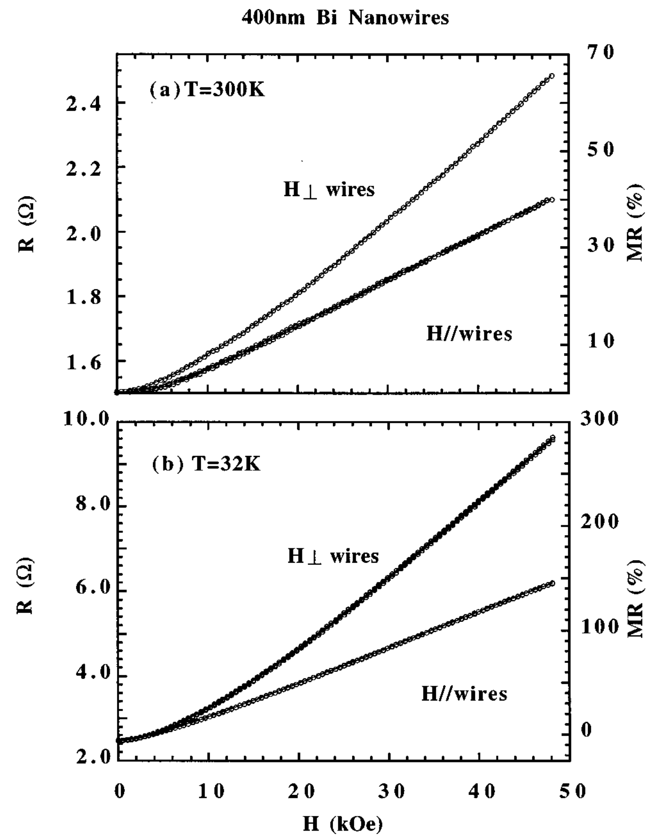

FIG. 3. Transverse ($H\perp$) and longitudinal ($H\|$) magnetoresistance of 400 nm Bi nanowires at (a) 300 K and (b) 32 K.

the carrier density, where ω_c is the cyclotron frequency, τ is the relaxation time. The ordinary MR exhibited in metals is usually very small, less than a few percent, owing to the very small values of $\omega_c\tau$. However, in semimetallic Bi, due to the very low carrier concentration, several orders of magnitude smaller than those in typical metals, the characteristic term $\omega_c\tau$ is much larger, leading to a large positive magnetoresistance. In pure bulk Bi single crystals, large values of MR have been observed at 4.2 K.[17] However, in thin films, other than the molecular-beam epitaxy grown epitaxial Bi single crystals,[16,18] the magnitude of the MR effect is generally much less.[14,19] As shown in this work, very large MR effect can be realized in arrays of Bi nanowires, fabricated by electrodeposition. The structural study by TEM has revealed that the Bi nanowires essentially consist of large grains along the wire direction. This should be contrasted to the much smaller grains found in the sputtered Bi films.[20] Such structural difference also contributes to the large MR observed in nanowires.

The large MR effect size in Bi nanowires and the linear field dependence at high fields and all temperatures are useful for wide-range field sensing. These attractive features notwithstanding, the field sensitivity needs to be enhanced for sensing at very low fields. Preliminary results with the incorporation of field concentrators into the nanowire structure have shown encouraging improvement on the field sensitivity. Finally, because of the nanowire geometry, field sensing is administered locally near the tip of the nanowire. This suggests the possibility of using Bi nanowire arrays with a controlled wire density as massive parallel-sensing systems in high-density perpendicular recording media, such as those of quantum disks.[21]

In summary, we have successfully fabricated arrays of semimetallic Bi nanowires using electrodeposition. Very large positive magnetoresistance, 300% at low temperatures and 70% at room temperature, with quasilinear field dependence have been observed. The one-dimensional nanostructures of semimetals show promise of a new medium for fruitful explorations of interesting phenomena and technological applications.

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